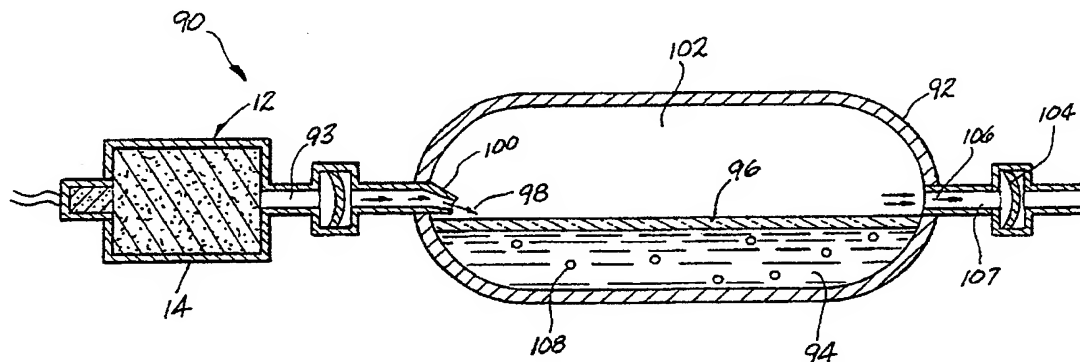




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : A62C 35/02, C06B 45/10	A1	(11) International Publication Number: WO 95/00205 (43) International Publication Date: 5 January 1995 (05.01.95)
(21) International Application Number: PCT/US94/06622 (22) International Filing Date: 13 June 1994 (13.06.94) (30) Priority Data: 082,137 24 June 1993 (24.06.93) US 248,932 25 May 1994 (25.05.94) US (71) Applicant: OLIN CORPORATION [US/US]; 350 Knotter Drive, P.O. Box 586, Cheshire, CT 06410-0586 (US). (72) Inventors: GALBRAITH, Lyle, D.; 13319 N.E. 12th Place, Redmond, WA 98052 (US). HOLLAND, Gary, F.; 20118-59th Avenue S.E., Snohomish, WA 98290 (US). POOLE, Donald, R.; 23327 77th Avenue S.E., Woodinville, WA 98072 (US). MITCHELL, Robert, M.; 24511 S.E. 39th Place, Issaquah, WA 98027 (US). (74) Agents: ROSENBLATT, Gregory, S. et al.; Wiggin & Dana, One Century Tower, New Haven, CT 06508-1832 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: APPARATUS AND METHOD FOR SUPPRESSING A FIRE**(57) Abstract**

There is disclosed a flame suppressing composition and an apparatus (90) for suppressing a fire. The composition contains a propellant and an effective amount of magnesium carbonate. One apparatus (90) directs the effluent (98) of a propellant (14) at a mixture of ice (96) and water (94) to generate superheated steam (106). Preferably, the effluent (98) is a mixture of hot gases and solid particulate directed by a nozzle (100) to impinge the mixture of ice (96) and water (94).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

APPARATUS AND METHOD FOR
SUPPRESSING A FIRE

This invention relates to an apparatus and a method for suppressing a fire. More particularly, a gas generator produces an elevated temperature first gas which interacts with a vaporizable liquid to generate a second gas having flame suppressing capabilities.

Fire involves a chemical reaction between oxygen and a fuel which is raised to its ignition temperature by heat. Fire suppression systems operate by any one or a combination of the following: (i) removing oxygen, (ii) reducing the system temperature, (iii) separating the fuel from oxygen, and (iv) interrupting the chemical reactions of combustion. Typical fire suppression agents include water, carbon dioxide, dry chemicals and the group of halocarbons collectively known as Halons.

The vaporization of water to steam removes heat from the fire. Water is an electrical conductor and its use around electrical devices is hazardous. However, in non-electrical situations, when provided as a fine mist over a large area, water is an effective, environmentally friendly, fire suppression agent.

Carbon dioxide (CO₂) gas suppresses a fire by a combination of the displacement of oxygen and absorption of heat. Carbon dioxide gas does not conduct electricity and may safely be used around electrical devices. The carbon dioxide can be stored as compressed gas, but requires high pressure cylinders for room temperature storage. The cylinders are heavy and the volume of compressed gas limited. Larger quantities of carbon dioxide are stored more economically as a liquid which vaporizes

-2-

when exposed to room temperature and atmospheric pressure.

When exposed to room temperature and atmospheric pressure, the expansion characteristics of liquid CO₂ are such that approximately one third of the vessel charge freezes during the blow down process. Only about two thirds of the CO₂ is exhausted in a reasonable time. The remainder forms a dry ice mass which remains in the storage vessel. While the dry ice eventually sublimates and exits the vessel, the sublimation period is measured in hours and is of little use in fire suppression.

The problem with liquid carbon dioxide based fire suppression systems is worse when low temperature operation is required. At -55°C, the vapor pressure of carbon dioxide is about 0.48 MPa (70 psig) (compared to 4.8 MPa (700 psig) at 20°C) which is totally inadequate for rapid expulsion. The vessel freeze-up problem is worse. About 50% of the liquid carbon dioxide solidifies when exposed to -55°C and atmospheric pressure.

Improved carbon dioxide suppression systems add pressurized nitrogen to facilitate the rapid expulsion of carbon dioxide gas at room temperature. The pressurized nitrogen does not resolve the freezing problem at low temperatures and at upper service extremes, about 70°C, the storage pressure is extremely high, dictating the use of thick, heavy, walled storage vessels.

Chemical systems extinguish a fire by separating the fuel from oxygen. Typical dry chemical systems include sodium bicarbonate, potassium bicarbonate, ammonium phosphate and potassium chloride. Granular

-3-

graphite with organic phosphate added to improve effectiveness, known as G-1 powder, is widely used on metal fires. Other suitable dry compounds include sodium chloride with tri-calcium phosphate
5 added to improve flow and metal stearates for water repellency, dry sand, talc, asbestos powder, powdered limestone, graphite powder and sodium carbonate. Dry chemical systems are delivered to a fire combined with a pressurized inert gas or
10 manually such as with a shovel. The distribution system is inefficient for large fires and a significant amount of time is required to deliver an effective quantity of the dry powder to suppress a large fire.

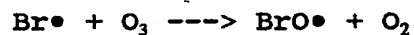
15 The most efficient fire suppression agents are Halons. Halons are a class of brominated fluorocarbons and are derived from saturated hydrocarbons, such as methane or ethane, with their hydrogen atoms replaced with atoms of the halogen
20 elements bromine, chlorine and/or fluorine. This substitution changes the molecule from a flammable substance to a fire extinguishing agent. Fluorine increases inertness and stability, while bromine increases fire extinguishing effectiveness. The
25 most widely used Halon is Halon 1301, CF_3Br , trifluorobromomethane. Halon 1301 extinguishes a fire in concentrations far below the concentrations required for carbon dioxide or nitrogen gas. Typically, a Halon 1301 concentration above about
30 3.3% by volume will extinguish a fire.

Halon fire suppression occurs through a combination of effects, including decreasing the available oxygen, isolation of fuel from atmospheric

-4-

oxygen, cooling and chemical interruption of the combustion reactions. The superior fire suppression efficiency of Halon 1301 is due to its ability to terminate the runaway reaction associated with combustion. The termination step is catalytic for Halon 1301 due to the stability of bromine radicals ($\text{Br}\cdot$) formed when Halon 1301 is disposed on a combustion source.

When unreacted Halon 1301 migrates into the stratosphere, sunlight breaks down the Halon 1301 forming bromine radicals. $\text{Br}\cdot$ then reacts to consume ozone in an irreversible manner.



In view of the current recognition that ozone depletion is a serious environmental problem, a move is on to identify: (i) fire suppression agents having a less severe environmental impact than Halon and (ii) devices to deliver these more environmentally friendly agents.

Accordingly, it is an object of the invention to provide a fire suppression apparatus for effectively delivering a fire suppressant which is less environmentally hazardous than Halon. It is a feature of the invention that the apparatus effectively delivers both liquid and solid fire suppressants. It is an advantage of the invention that the apparatus does not require significantly more space than Halon fire suppression apparatus. A further advantage of the invention is that both high and low vapor pressure liquids are effectively stored, vaporized and delivered in gaseous form.

-5-

In accordance with the invention, there is provided an apparatus for suppressing a fire. The apparatus contains a gas generator and a vaporizable liquid contained within a chamber. A passageway is provided between the chamber and a fire. When activated, the apparatus suppresses a fire by generating an elevated temperature first gas. A first liquid is substantially vaporized by interaction with the first gas generating a second gas having flame suppressing capabilities, the second gas is then directed at the fire.

In another embodiment of the invention, the first gas is an effective flame suppressant such as CO₂, N₂ or water vapor. The first gas may be used directly as a flame suppressant or combined with the second gas for flame suppression.

The above stated objects, features and advantages will become more apparent from the specification and drawings which follow.

Figure 1 illustrates in cross-sectional representation an apparatus for vaporizing a liquid to a flame suppressing gas in accordance with a first embodiment of the invention.

Figure 2 illustrates in cross-sectional representation an apparatus for vaporizing a liquid to a flame suppressing gas in accordance with a second embodiment of the invention.

Figure 3 illustrates in cross-sectional representation an apparatus for delivering a dry chemical flame suppressant to a fire.

Figure 4 illustrates in cross-sectional representation a carbon dioxide producing gas generator.

-6-

Figure 5 graphically illustrates increasing the magnesium carbonate content in the gas generator reduces the formation of corrosive effluent.

Figure 6 graphically illustrates the
5 relationship between pressure and density for ice and water.

Figure 7 illustrates in cross sectional representation a water based fire suppression system in accordance with the invention.

10 Figure 1 shows in cross-sectional representation a fire suppression apparatus 10 in accordance with a first embodiment of the invention. A gas generator 12 containing a suitable solid propellant 14 delivers an elevated temperature first gas 16 to a
15 vaporizable liquid 18 contained in a chamber 20. A first conduit 22 provides a passageway between the gas generator 12 and the chamber 20. The first gas 16 interacts with the vaporizable liquid 18 converting the liquid to a second gas 24. By proper
20 selection of the vaporizable liquid 18, the second gas has flame suppressing capabilities. A second conduit 26 directs the second gas 24 to a fire. An optional aspirator 28 uniformly distributes the second gas 24 over a wide area.

25 The fire suppression apparatus 10 is permanently mounted in a ceiling or wall of a building, aircraft or other suitable structure or vehicle. A sensor 30 detects the presence of a fire. Typically, the sensor 30 detects a rise in temperature or a change
30 in the ionization potential of air due to the presence of smoke. On detecting a fire, the sensor 30 transmits an activating signal to a triggering mechanism 32. The activating signal may be a radio

-7-

pulse, electric pulse transmitted by wires 34 or other suitable means.

The triggering mechanism 32 is any device capable of igniting the solid propellant 14. One triggering mechanism is an electric squib. The electric squib has two leads interconnected by a bridge wire, typically 0.076mm-0.10mm (3-4 mil) diameter nichrome. When a current passes through the leads, the bridge wire becomes red hot, igniting an adjacent squib mixture, typically, zirconium and potassium perchlorate. The ignited squib mixture then ignites an adjacent black powder charge, creating a fire ball and pressure shock wave which ignites the solid propellant 14 housed within the gas generator 12.

The gas generator 12 contains a solid propellant 14 which on ignition generates a large volume of a high temperature gas containing fire suppressing fluids such as carbon dioxide, nitrogen and water vapor. Depending on the selection of the vaporizable liquid and the type of fire anticipated as requiring suppression, the gas is generated for a period of time ranging from a few milliseconds to several seconds. One particularly suitable gas generator is the type used in automotive air bags as described in U.S. Patent No. 3,904,221 to Shiki et al. A housing 36 supports the solid propellant 14 and directs an explosive shock wave in the direction of the vaporizable liquid 18. Typical materials for the housing 36 include aluminum alloys and stainless steel.

The preferred solid propellant 14 is a combustible mixture which generates a copious amount

-8-

of high temperature gas. The chemical reactions converting the propellant to the first gas generally do not occur efficiently at temperatures below about 1093°C (2000°F). The gas yield in moles per 100
5 grams of propellant should be in excess of about 1.5 moles and preferably in excess of about 2.0 moles. The propellants are generally a mixture of a nitrogen rich fuel and an oxidizing agent in the proper stoichiometric ratio to minimize the
10 formation of hydrogen and oxygen. The preferred fuels are guanidine compounds, azide compounds and azole compounds.

Two preferred solid propellants are "RRC-3110" and "FS-01" (both available from Olin Aerospace
15 Company of Redmond, Washington, United States of America). The compositions (in weight percent) of these propellants are:

RRC-3110

	5-Aminotetrazole	28.62%
20	Strontium nitrate	57.38%
	Clay	8.00%
	Potassium 5-Aminotetrazole	6.00%

When ignited, RRC-3110 generates H₂O, N₂ and CO₂ as well as SrO, SrCO₃ and K₂CO₃ particulate.

25 FS-01

	5-Aminotetrazole	29.20%
	Strontium nitrate	50.80%
	Magnesium carbonate	20.00%

When ignited, FS-01 generates H₂O, N₂ and CO₂ as
30 well as SrO, SrCO₃ and MgO particulate.

-9-

Another useful propellant composition is:

Guanidine nitrate	49.50%
Strontium nitrate	48.50%
Carbon	2.00%

- 5 When ignited, this composition releases a mixture of H_2O , N_2 and CO_2 gases along with SrO and $SrCO_3$ particulate solids.

- Propellants which generate KCl salt are also suitable. KCl is effective in suppressing fires, but the corrosive nature of the salt limits the application of these propellants. Two such propellants are:

5-Aminotetrazole	30.90%
Potassium perchlorate	44.10%
15 Magnesium carbonate	25.00%

When ignited, this propellant generates H_2O , N_2 and CO_2 gas as well as KCl and MgO particulate.

Potassium chlorate	61.0%
Carbon	9.0%
20 Magnesium carbonate	30.0%

When ignited, this propellant generates CO_2 as the only gas and KCl and MgO particulate.

- Another suitable propellant generates nitrogen gas and solid slag which remains in the housing 36, only the gas is delivered to the vaporizable liquid eliminating contamination of the area by the solid particulate.

Sodium azide	59.1%
Iron oxide	39.4%

-10-

Potassium nitrate	1.0%
Carbon	0.5%

When ignited, this propellant generates N_2 gas and slag which is not discharged from the housing.

5 The propellants useful in the apparatus of the invention are not limited to the five specified above. Any solid propellant capable of generating similar gaseous products at high velocity and high temperature is suitable.

10 The most preferred propellants contain magnesium carbonate as a suppressing agent. The magnesium carbonate may be combined with a fuel, as in the FS-01 propellant, combined with other suppressing agents or utilized as a single component fire
15 suppressing propellant. The magnesium carbonate endothermically decomposes to carbon dioxide (a good oxygen displacer) and magnesium oxide (a good heat sink and coolant).

20 Suitable propellants contain from that amount effective to extinguish a fire up to about 95% by weight magnesium carbonate and the balance being the mixture of a fuel and an oxidizer. Preferably, the propellant contains from about 20% to about 70% by weight magnesium carbonate and most preferably, from
25 about 30% to about 60% by weight magnesium carbonate.

30 When the magnesium carbonate content is low, propellants containing strontium nitrate yield effluent rich in strontium oxide. On exposure to atmospheric moisture, this yields extremely basic solutions that are corrosive to aluminum and other materials utilized in aircraft manufacture. With

-11-

reference to Figure 5, applicant has determined a minimum magnesium carbonate content of about 35% is desired to minimize the corrosion potential.

Propellant additives such as magnesium carbonate
5 act as endothermic heat sinks and carbon dioxide generators. These effects decrease the corrosivity of propellant effluent by minimizing the amount of strontium oxide generated. Figure 5 graphically illustrates the composition of the gaseous effluent
10 generated by igniting the FS-01 fuel with varying amounts of magnesium carbonate present. The strontium oxide content is identified by reference line 80. Approximately 35 weight percent magnesium carbonate is required to achieve an essentially
15 strontium oxide free effluent.

Strontium carbonate (reference line 82) and magnesium oxide (reference line 84) form compounds with a pH near 7 when exposed to atmospheric moisture and generally do not cause significant
20 corrosion.

A preferred propellant contains a nitrogen rich fuel, an oxidizer and magnesium carbonate. Suitable propellants include modifications of FS-01 containing 5-aminotetrazole and an oxidizer, such as
25 strontium nitrate, potassium perchlorate or mixtures thereof. The fuel to oxidizer ratio, by weight, is from about 1:1 to about 1:2. Combined with the fuel and oxidizer is from about 20% to about 70% by weight magnesium carbonate (measured as a percentage
30 of the propellant/magnesium carbonate/additives compacted mixture). The propellant may also contain additives such as clay (to improve molding

-12-

characteristics) or graphite (to improve flow characteristics).

The propellant is a mixture of compacted powders. If all powder components are approximately the same size, the burn rate is unacceptably low. Preferably, the propellant is a mixture of relatively large magnesium carbonate particles having an average particle diameter of from about 150 microns to about 200 microns and relatively small fuel and oxidizer particles having an average particle diameter of from about 50 microns to about 75 microns. The larger magnesium carbonate particles form discrete coolant sites and do not reduce the propellant burn rate as drastically as when all components are approximately the same size.

The solid propellant may be required to generate the gas over a time ranging from about 30 milliseconds to several seconds. Typically, a short "burn time" is required in an explosive environment while a longer burn time is required in a burning environment. If a short burn time is desired, the propellant is in the form of tablets, typically on the order of 1 centimeter in diameter by about one half centimeter thick. Increasing the pellet size increases the burn time. For a burn time of several seconds, the gas generator contains a single propellant slug compression molded into the housing.

Referring back to Figure 1, to prevent the housing 36 from melting during ignition of the solid propellant 14, a cooling material 38 may be disposed between the housing 36 and solid propellant 14. One cooling material is granular magnesium carbonate which generates carbon dioxide when heated above

-13-

150°C (300°F). One mole of MgCO_3 will produce one mole of CO_2 plus one mole of MgO , which remains in the housing 36 in the form of a slag. Small amounts of MgO dust may be exhausted during ignition of the solid propellant.

To prevent contamination of the chamber 20 by the solid propellant 14 prior to ignition, a first rupture diaphragm 40 isolates the vaporizable liquid 18. The isolation diaphragm 40 is ruptured by the pressure of the shock wave. No active device such as a disk rupturing detonator is required. To prevent the generation of mechanical debris, the isolation diaphragm 40 may have score lines and hinge areas to open in a petal like fashion.

The first conduit 22 forms a passageway to communicate the first gas 16 to the vaporizable liquid 18. The first gas 16 is superheated and traveling at high velocity. Interaction of the first gas and the vaporizable liquid 18 vaporizes the liquid, generating a second gas 24. The second gas 24 ruptures the second isolation diaphragm 42 and is expelled as a fire suppressing gas, preferably through aspirator 28.

The selection of the vaporizable liquid 18 is based on a desire that the second gas 24 be less reactive with atmospheric ozone than Halon. The vaporizable liquid 18 contains no bromine, and preferably also no chlorine. Preferred groups of vaporizable liquids 18 include fluorocarbons, molecules containing only a carbon-fluorine bond and hydrogenated fluorocarbons, molecules containing both carbon-hydrogen and carbon-fluorine bonds. Table 1 identifies preferred fluorocarbons and

-14-

hydrogenated fluorocarbons and their vaporization temperatures. For comparison, the data for Halon 1301 is also provided.

TABLE 1

System	Formula	Vaporization Temperature (°C)	Vaporization Pressure	
			Room Temperature	
			(MPa)	(psi)
HFC-32	CH ₂ F ₂	-52	0.83	120
HFC-227	CF ₃ CHFCH ₃	-15	0.41	59
10 HCFC-22	CHClF ₂	-41	0.96	139
HCFC-134A	CF ₃ CH ₂ F	-27	0.57	83
FC-116	CF ₃ CF ₃	-78	3.2	465
HCFC-124	CHClFCF ₃	-12	0.42	61
HFC-125	CF ₃ CF ₂ H	-48	1.3	195
15 FC31-10	C ₄ F ₁₀	- 2	—	—
FC-C318	(CF ₂) ₄	- 4	—	—
HF-23	CF ₃ H	-82	4.8	700
HCFC-123	CF ₃ CCl ₂ H	-28	0.09	13
FC-218	CF ₃ CF ₂ CF ₃	-36	0.83	120
20 FC-614	C ₆ F ₁₄	+56	—	—
HALON 1301	CF ₃ Br	-58	1.5	220

The most preferred fluorocarbons and hydrogenated fluorocarbons are those with the higher boiling points and lower vapor pressures. The higher boiling point reduces the pressure required to store the vaporizable liquid 18 as a liquid. The lower vapor pressures increase the rate of conversion of the vaporizable liquid to fire suppressing gas on ignition. Particularly suitable are HFC-227, FC-31-10, FC-318 and FC-218.

Unsaturated or alkene halocarbons have a low vapor pressure and a relatively high boiling point.

-15-

These unsaturated molecules contain a carbon-carbon double bond, together with a carbon-fluorine bond, and in some cases, a carbon-hydrogen bond. The unsaturation causes these compounds to be considerably more photosensitive than a saturated species, leading to significant photochemical degradation in the lower atmosphere. The low altitude photodegradation may lessen the contribution of these compounds to stratospheric ozone depletion. Through the use of an unsaturated halocarbon in the fire suppression apparatus of the invention, it is possible that bromine containing compounds may be tolerated.

Representative haloalkenes have a boiling point of from about 35°C to about 100°C and include 3-bromo-3,3-difluoro-propene, 3-bromo-1,1,3,3-tetrafluoropropene, 1-bromo-3,3,3-trifluoro-1-propene, 4-bromo-3,3,4,4-tetrafluoro-1-butene and 4-bromo-3,4,4-trifluoro-3-(trifluormethyl)-1-butene, as well as homologues, analogs and related compounds.

One disadvantage with the fluorocarbons and hydrogenated fluorocarbons, whether saturated or unsaturated, is the generation of small amounts of hydrogen fluoride when the vapor contacts a fire. Hydrogen fluoride is corrosive to equipment and hazardous to personnel.

The significant heat and pressure conducted by the first gas 16 permits the use liquid carbon dioxide or water as the vaporizable liquid 18. The expansion problem identified above for nonenergetically discharged liquid carbon dioxide is eliminated by the superheating effect of the first

-16-

gas 16. Water is converted to a fine mist of steam on interaction with the first gas and is highly effective for flame suppression.

As water is such an effective fire suppression media when delivered in the form of fine droplets, a mist or as a superheated steam to a fire, it is one of the most favored fluids for use in this gas generation concept. However, because water freezes at a temperature of 0°C (32°F), a means must be incorporated to either suppress the freezing point or the design of the gas generator must be such that it can operate effectively with the water frozen solid.

Most military and commercial applications require that fire suppression equipment operate effectively over a temperature range of -54°C to +71°C (-65°F to +160°F). Many additives such as ammonia, alcohol, glycols, and salts are capable of suppressing the water freezing point to below -54°C (-65°F), but a considerable portion of the mixture becomes the additive. Most additives are flammable or corrosive, degrading the effectiveness and desirable features of a water system when freezing point depressants are present in the water.

To maintain the desirable features of water as the agent for the gas generator driven system, the system can be designed to operate effectively over the desired -54°C to +71°C (-65°F to +160°F) temperature range even if the water has frozen solid.

Figure 6 graphically illustrates the relationship between density and temperature for water and ice at atmospheric pressure, moderate

-17-

increased pressure and moderate vacuums. At slightly over 0°C (+32°F), the density of liquid water is 1.0 g/cm³ (62.40 lbm/ft³). If the temperature of the water is reduced just below 0°C (32°F), the water will freeze to ice and expand considerably in volume. The density of ice at 0°C (+32°F) is 0.92 g/cm³ (357.50 lbm/ft³).

Below 0°C, the density of ice increases as the temperature is decreased as illustrated by reference line 86. Above 0°C, the density of water decreases as the temperature is increased as illustrated by reference line 88.

Figure 7 shows in cross sectional representation a water based fire suppression system 90 that accommodates the expansion of ice due to freezing the water. The fire suppression system 90 includes a solid propellant gas generator 12 described above and previously illustrated in Figure 1. The gas generator 12 communicates with a tank 92 by a passageway formed by a first conduit 93. The tank 92 contains a mixture of water 94 and ice 96. The tank 92 has a volume larger than the volume of ice that would be contained if all the water 94 was frozen.

The gas generator 12 provides sufficient thermal energy to heat the ice 96 to the freezing point and melt the ice by directing a hot gas 98 produced by the gas generator 12 in the direction of the ice 96. Nozzle 100 may be provided to direct the flow of the hot gas 98 to impinge the mixture of ice and water inducing turbulence to assure good mixing and vaporization of the water.

-18-

Heating of the ice 96 and water 94 is further enhanced by the use of a propellant which exhausts a significant percent of solids into the tank 92 along with the hot gases 98. Preferably, at least about
5 20% by weight, and most preferably, at least about 40% by weight of the effluent is solid particles.

The tank 92 is designed to facilitate unrestricted expansion of ice 96. There are no pockets or cavities to interfere with the ice
10 growth. Mechanical parts of the gas generator are not in the path of ice growth to minimize breaking of the mechanical parts.

The temperature of the generated gases is preferably in excess of about 925°C (1700°F) and
15 typically exceeds 1093°C (2000°F). The gas generator is preferably selected so that the exhaust contains at least 20% and preferably in excess of about 40% by weight hot solid particulate (i.e. MgO, etc.). This exhaust stream provides a very
20 effective means for rapidly melting the ice.

Another feature of the water based fire suppression system 90 is that the ullage space 102 above the water 94 and ice 96 is sufficiently large to assure that the resulting pressure of the hot
25 gases 98 exhausting into the tank 92 do not produce a pressure sufficient to rupture the outlet burst disc 104, typically about 13.8 MPa (2000 psig). The system is designed to require additional hot gases 98 from the gas generator 92 to be added to
30 superheat the vaporized water before the outlet disc 104 is ruptured and flow commences.

Once the outlet disc 104 has been ruptured, the continuing flow of gases 98 from the gas generator

-19-

12 creates significant turbulence and mixing of the water 94 within the tank 92 vaporizing the water to produce steam 106. Depending upon the particular fire suppressing application, it may be desirable to design the unit to produce low quality steam at low temperatures or superheated steam at higher temperatures. Any temperature and steam quality can be produced by the proper proportioning of the water and solid propellant used in the system. The steam 106 is directed at the fire through a second passageway formed by a second conduit 107.

It is sometimes be desirable to incorporate an additive 108 to the water 94 to reduce the heat of fusion of the ice 96. Effective chemical additives include polyvinyl alcohol and water soluble polymers such as methyl cellulose, added to the water in concentrations of less than about 15% by volume. The additives 108 also tend to form a viscous gel when properly added to the water. This higher viscosity working fluid is much less prone to leaking from the tank 92 than water.

In a second embodiment of the invention, the fire suppression apparatus 50 is as illustrated in cross-sectional representation in Figure 2. The elements of the second fire suppression apparatus 50 are substantially the same as those illustrated in Figure 1 and like elements are identified by like Figure numerals. Typically the solid propellant 14 generates solid particulate along with the first gas. Particulate may be also be generated by other components of the fire suppression apparatus such as the magnesium carbonate cooling layer 38. If the environment in which the flame suppression apparatus

-20-

50 is located would be detrimentally effected by the presence of solid particulate, a bladder 52 may be disposed between the gas generator 12 and the chamber 20. The energetic first gas 16 forcedly
5 deforms the flexible bladder 52, generating a shock wave vaporizing the vaporizable liquid 18 and generating the second gas 24. The bladder 52 may be any suitable material such as a high temperature elastomer.

10 This second embodiment does not superheat the vaporizable liquid 18 as effectively as the first embodiment. The transfer of heat through the elastomeric material 52 is limited. Accordingly, lower boiling point vaporizable liquids such as
15 HFC-32, FC-116 and HF-23 are preferred.

In a third embodiment of the invention, a solid flame suppressant may be utilized as illustrated by the flame suppression apparatus 60 of Figure 3. The flame suppression apparatus 60 illustrated in
20 cross-sectional representation is similar to the earlier embodiments and like elements are identified by like reference numerals, while elements performing a similar function are identified by primed reference numerals. The chamber 20' is
25 packed with small diameter, on the order of from about 5 to about 100 micron, and preferably from about 10 to about 50 micron, particles 62 of any effective flame suppressing material. Suitable materials include potassium bicarbonate, sodium
30 bicarbonate, ammonium phosphate, potassium chloride, granular graphite, sodium chloride, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, aluminum hydroxide, magnesium

-21-

carbonate, potassium sulfate, sand, talc, powdered limestone, graphite powder, sodium carbonate, strontium carbonate, calcium carbonate and magnesium carbonate. These and other suitable materials may
5 be mixed with boron oxide as disclosed in U.S. Patent No. 4,915,853 to Yamaguchi.

In the preceding embodiments of the invention, the flame suppression apparatus has been described in terms of a superheated gas interacting with a
10 vaporizable liquid. The superheated gas is predominantly nitrogen, carbon dioxide and water vapor, all effective fire suppressants. In certain applications, it is preferred to omit the vaporizable liquid and discharge the flame
15 suppressing gases generated by the solid propellant directly onto the fire. A carbon dioxide producing gas generator 70 is illustrated in cross-sectional representation in Figure 4.

The carbon dioxide producing gas generator 70 is
20 similar to the gas generators described above. An electric squib 32 activates an energetic mixture of a solid propellant 14. On ignition, the solid propellant 14 ignites a magnesium carbonate containing propellant 72 generating MgO, CO₂, N₂, and
25 water vapor. A perforated screen 74 separates the propellants from the housing 12. A magnesium carbonate cooling bed 76 is disposed between the housing 12 and propellants and on heating generates additional CO₂. The propellant 72 may contain other
30 fire suppressing agents, in addition to magnesium carbonate, either alone or in combination. Suitable fire suppressing agents include magnesium hydroxide,

-22-

calcium hydroxide, strontium hydroxide, barium hydroxide and aluminum hydroxide.

The following examples illustrates the effectiveness of the flame suppressing apparatus of the invention.

EXAMPLES

Example 1

The gas generator 70 is an efficient apparatus for delivering a low molecular weight inerting agent, such as CO₂, N₂, or water vapor, to a fire. The weight of the apparatus and propellant compares favorably to the weight of a halon based fire suppression system.

Gas Generator Characteristics

Length - 42.24 centimeters (16.63 inches)
Diameter - 13.97 centimeters (5.50 inches)
Displaced external volume - 0.0065 meter³ (395 inch³)
FS-O1 propellant load - 2.01 kilograms (4.437 pounds), generates 1.41 kilograms (3.10 pounds) of CO₂, N₂, and water vapor
MgCO₃ coolant load - 6.00 kilograms (13.21 pounds), generates 3.13 kilograms (6.894 pounds) of CO₂)
Total inerting gas produced - 4.54 kilograms (10.00 pounds)
Estimated weight of total system - 11.8 kilograms (26.10 pounds)

Gas Generator Materials

Housing 12 - Aluminum alloy 6061-T6
Solid propellant 14 - BKNO₃

-23-

FS-01 propellant 72 - in pellet form, size of pellets based

on desired burn time, about 1 centimeter diameter by 0.5 centimeter thick tablets provide
5 a 30 millisecond burn.

MgCO₃ coolant bed 76 - granular

Perforated retaining screen 74 has 1.27 millimeter (0.050 inch) perforations.

This system will produce about 4.54 kilograms
10 (10 pounds) of CO₂, N₂, and water vapor, weigh about 11.8 kilograms (26.10 pounds) and occupy 0.0065 meter³ (395 inch³) of space. By comparison, a Halon 1301 system containing 4.54 kilograms (10 pounds) of fire suppressant weighs about 8.6 kilograms (19
15 pounds) and occupies 0.0065 meter³ (365 inch³) of space. While the system of the invention is only slightly larger and heavier than the Halon system, other Halon replacement systems are predicted to increase the weight by a factor of 2 or 3.

20 Example 2

The corrosive action of saturated solutions of the effluent components on materials commonly utilized in aircraft was evaluated. An aqueous solution saturated with the effluent was prepared
25 and the pH measured. Various materials were then exposed to a 50% relative humidity atmosphere of each saturated solution. After a 30 day exposure, the coupons were analyzed for corrosion pits. Table 2 illustrates the benefit of removing strontium
30 oxide from the effluent.

It is apparent that there has been provided in accordance with this invention an apparatus and

-24-

method for suppressing a fire which fully satisfies the objects, means and advantages set forth hereinbefore. While the invention has been described in combination with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the claims.

-25-

TABLE 2

	Composition	MgO	SrCO ₃	FS-01 40% MgCO ₃	FS-01 20% MgCO ₃	3110	SrO	KOH
pH (measured) Sat. Aq. Soln.		8.5	9.0	9.0	11.0	11.5	13.5	13.5
A06061 chromated surface	Mg 0.8-1.2 Si 0.4-0.8 Cu 0.15-0.40 Cr 0.04-0.34 Al Balance	not analyzed	not analy- zed	0	uniform pitting	uniform pitting	uni- form pit- ting	uni- form pit- ting
A07075 anodized surface	Zn 5.1-6.1 Mg 2.1-2.9 Cu 1.2-2.0 Cr 0.18-0.35 Al Balance	0	0	0	0	0	3	3
A07050 anodized surface	Zn 2.7-3.3 Mg 1.4-1.8 Mn 0.4-0.6 Cr 0.2-0.4 Al Balance	0	0	0	2	5	uni- form pit- ting	0
Ti-6Al-4V bare surface	Al 6 V 4 Ti Balance	0	0	0	0	0	0	0
A07075 bare surface		0	0	0	not analyzed	not analyzed	10	50

-26-

TABLE 2 (Continued)

	Composition	MgO	SrCO ₃	FS-01 40% MgCO ₃	FS-01 20% MgCO ₃	3110	SrO	KOH
A07050 bare surface		0	0	0	not analyzed	not analyzed	24	94
Graphite/Epoxy		0	0	0	0	0	0	0
Kevlar	Poly (p-phenylene- diamine-co- terephthalic) acid	0	0	0	0	0	0	0

-27-

IN THE CLAIMS:

1. An Apparatus (10,50) for suppressing a fire, characterized by:

- (a) a gas generator (12);
- 5 (b) a vaporizable liquid (18) contained within a chamber (20); and
- (c) a passageway (26) between said chamber (20) and said fire.

2. The apparatus (10,50) of claim 1
10 characterized in that said gas generator (12) generates a high temperature gas (16) selected from the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof.

3. The apparatus (10,50) of claim 2
15 characterized in that said gas generator (12) contains an effective mixture of 5-aminotetrazole, strontium nitrate, clay and potassium 5-aminotetrazole.

4. The apparatus (10,50) of claim 2
20 characterized in that said vaporizable liquid (18) is selected from the group consisting of fluorocarbons, hydrogenated fluorocarbons, haloalkenes, carbon dioxide, water and mixtures thereof.

-28-

5. The apparatus (10,50) of claim 4 characterized in that said vaporizable liquid (18) is a fluorocarbon having a boiling temperature below about -25°C and a room temperature vaporization pressure above about 0.17 MPa (25 psi).

6. The apparatus (10,50) of claim 2 characterized in that said vaporizable liquid (18) is selected from the group consisting of water and carbon dioxide.

7. The apparatus (50) of claim 2 further including an elastomeric bladder (52).

8. An apparatus (60) for suppressing a fire, characterized by:

- a) a gas generator (12);
- 15 b) a packed powder (62) contained within a chamber (20') and selected from the group consisting of magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, aluminum hydroxide, magnesium carbonate, potassium sulfate and mixtures thereof;
- 20 c) a first conduit providing a passageway between said gas generator (12) and said chamber (20'); and
- 25 d) a second conduit providing a passageway between said chamber (20') and said fire.

-29-

9. The apparatus (60) of claim 8 characterized in that said gas generator (12) contains a mixture of a nitrogen rich fuel and an oxidizer in a fuel to oxidizer ratio, by weight, of from about 1:1 to about 1:2.

10. The apparatus (60) of claim 9 characterized in that said fuel is 5-aminotetrazole and said oxidizer is selected from the group consisting of strontium nitrate, potassium chlorate and mixtures thereof.

11. The apparatus (60) of claim 9 characterized in that said packed powder (62) is selected from the group consisting of sodium bicarbonate, potassium bicarbonate, and mixtures thereof.

12. An apparatus (70) for suppressing a fire, characterized by:

a gas generator (12) containing a propellant (14) and a fire suppressant (72) which generates a high temperature gas selected from the group consisting of nitrogen, carbon dioxide, water vapor and mixtures thereof; and

a passageway between said gas generator (12) and said fire.

13. The apparatus (70) of claim 12 characterized in that said gas generator (12) contains a mixture of a nitrogen rich fuel and an oxidizing agent.

-30-

14. The apparatus (70) of claim 13
characterized in that said fire suppressant (72) is
selected from the group consisting of magnesium
carbonate, magnesium hydroxide, calcium hydroxide,
5 strontium hydroxide, barium hydroxide, aluminum
hydroxide, potassium sulfate and mixtures thereof.

15. The apparatus (70) of claim 14
characterized in that said propellant (14) and said
fire suppressant (72) are a mixture of compacted
10 powders and the average diameter of a fire
suppressant particle (72) is larger than the average
diameter of a propellant particle (14).

16. The apparatus (70) of claim 15
characterized in that said propellant (14) is a
15 mixture of a nitrogen rich fuel and an oxidizer in a
fuel to oxidizer ratio, by weight, of from about 1:1
to about 1:2.

17. The apparatus (70) of claim 16
characterized in that said fuel is 5-aminotetrazole
20 and said oxidizer is selected from the group
consisting of strontium nitrate, potassium chlorate
and mixtures thereof.

18. The apparatus (70) of claim 17
characterized in that the flame suppressant (72)
25 content is sufficient to inhibit the generation of
corrosive effluent by-products.

-31-

19. The apparatus (70) of claim 18 characterized in that said flame suppressant (72) contains from about 30% to about 60% by weight magnesium carbonate.

5 20. An apparatus (90) for suppressing a fire, characterized by:

 a gas generator (12) containing a propellant (14) and a fire suppressant;

 a first conduit (93) providing a passageway
10 between said gas generator (12) and a tank (92), said tank (92) containing a mixture of water (94) and ice (96); and

 a second conduit (107) providing a passageway between said tank (92) and said fire.

15 21. The apparatus (90) of claim 20 characterized in that said propellant (14) generates an effluent mixture of hot gases (98) and solid particulate.

 22. The apparatus (90) of claim 21
20 characterized in that said hot gases (98) have a temperature in excess of about 925°C and said mixture contains in excess of 20% by weight solid particulate.

 23. The apparatus (90) of claim 22
25 characterized in that said solid particulate is MgO.

-32-

24. The apparatus (90) of claim 21
characterized in that an outlet burst disc (104) is
incorporated into said second conduit (107), said
outlet burst disc (104) having a rupture pressure
5 effective to cause said hot gases (98) to vaporize
and superheat said water (94).

25. The apparatus (90) of claim 22
characterized in that said first conduit (93)
terminates at a nozzle (100) configured to impinge
10 said hot gases (98) and solid particulate on said
mixture of ice (96) and water (94).

26. The apparatus (90) of claim 22
characterized in that an additive (108) effective to
reduce the heat of fusion of ice (96) is present in
15 said water (94).

27. The apparatus (90) of claim 26
characterized in that said additive (108) is
selected from the group consisting of polyvinyl
alcohol and methyl cellulose.

20 28. A flame suppressing composition,
characterized by:
a propellant; and
from that amount effective to extinguish a
fire to about 95% by weight magnesium carbonate.

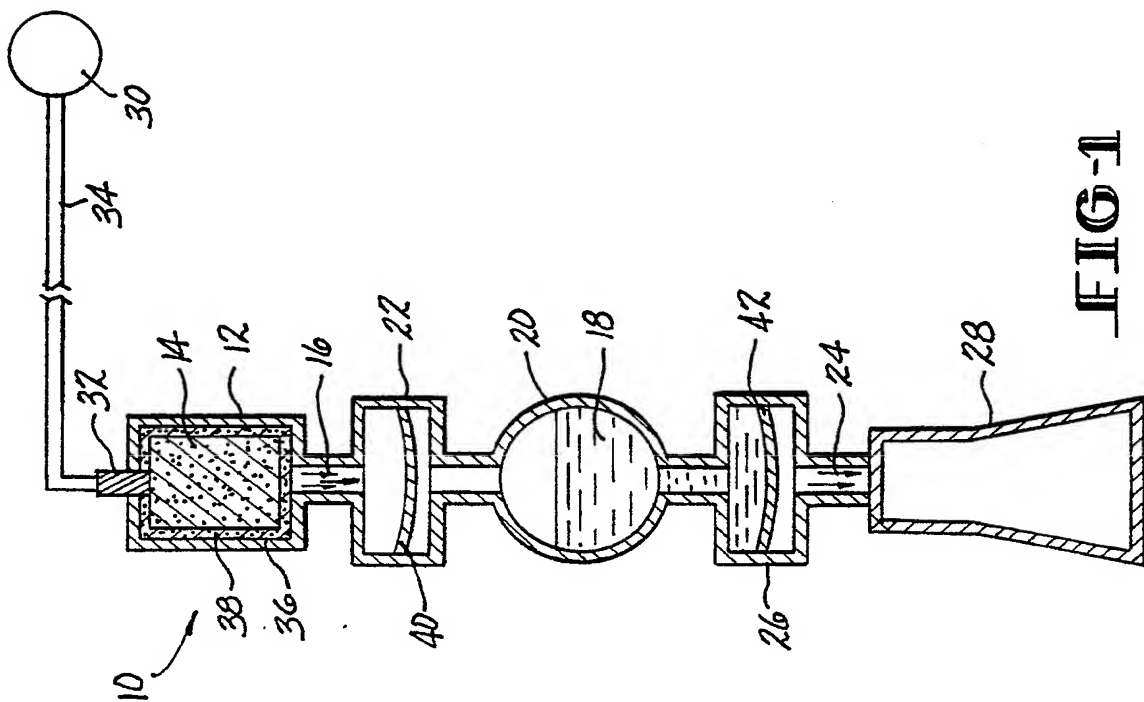
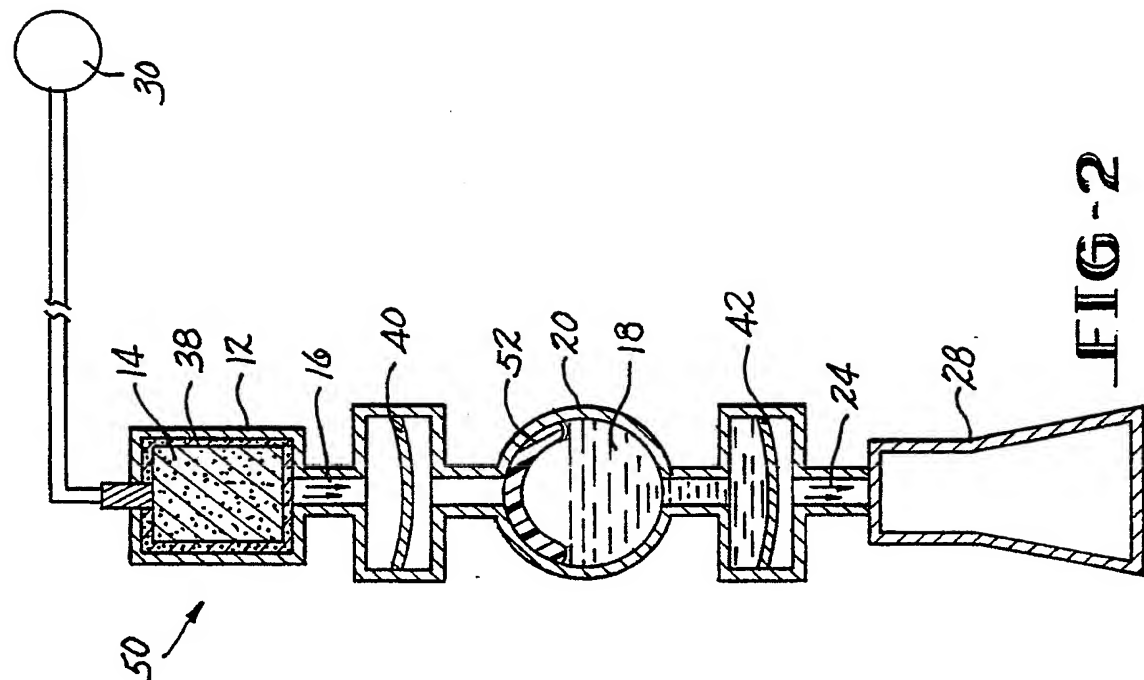
25 29. The flame suppressing composition of claim
28 characterized in that the magnesium carbonate
content is from about 20% to about 70% by weight.

-33-

30. The flame suppressing composition of claim 29 characterized in that said propellant is a mixture of a nitrogen rich fuel and an oxidizer in a fuel to oxidizer ratio, by weight, of from about 1:1 to about 1:2.

31. The flame suppressing composition of claim 29 characterized in that said propellant and said magnesium carbonate are a compacted mixture of powders and, on average, the magnesium carbonate particles are larger than propellant particles.

32. The flame suppressing composition of claim 30 characterized in that said fuel is guanidine nitrate.



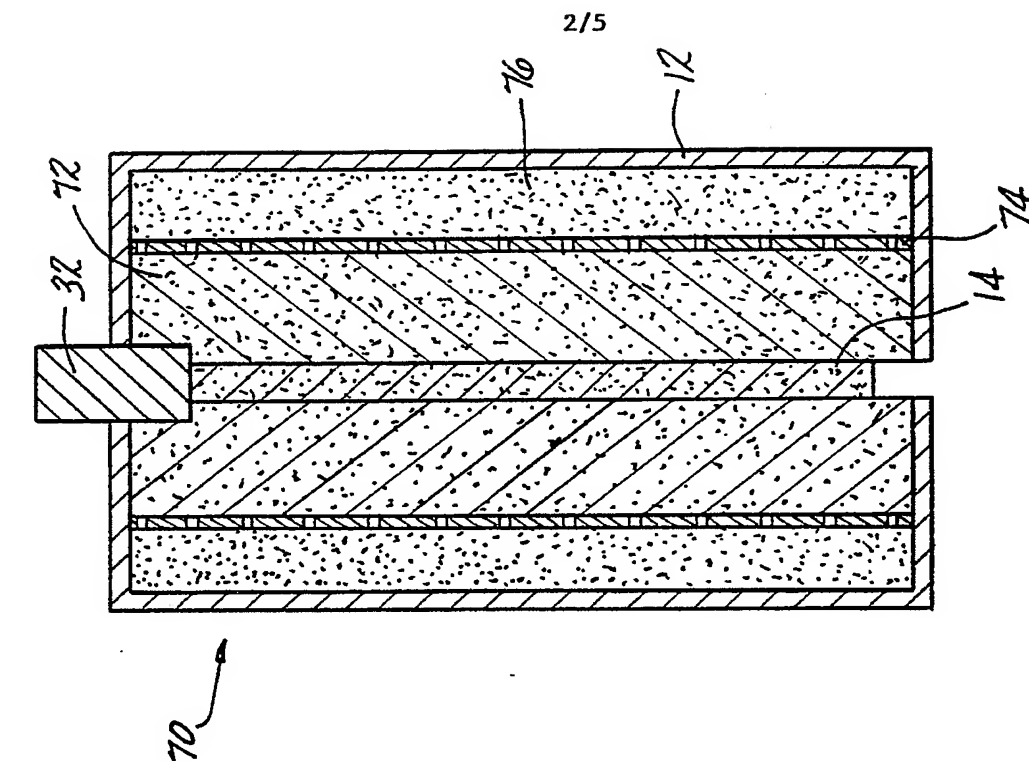
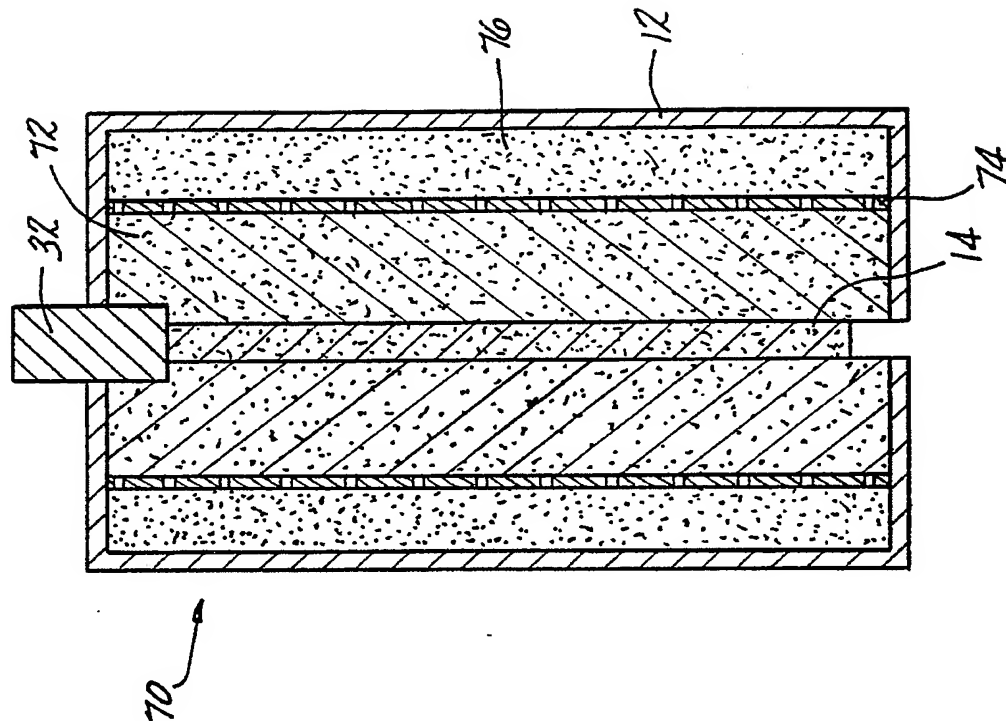


FIG-4



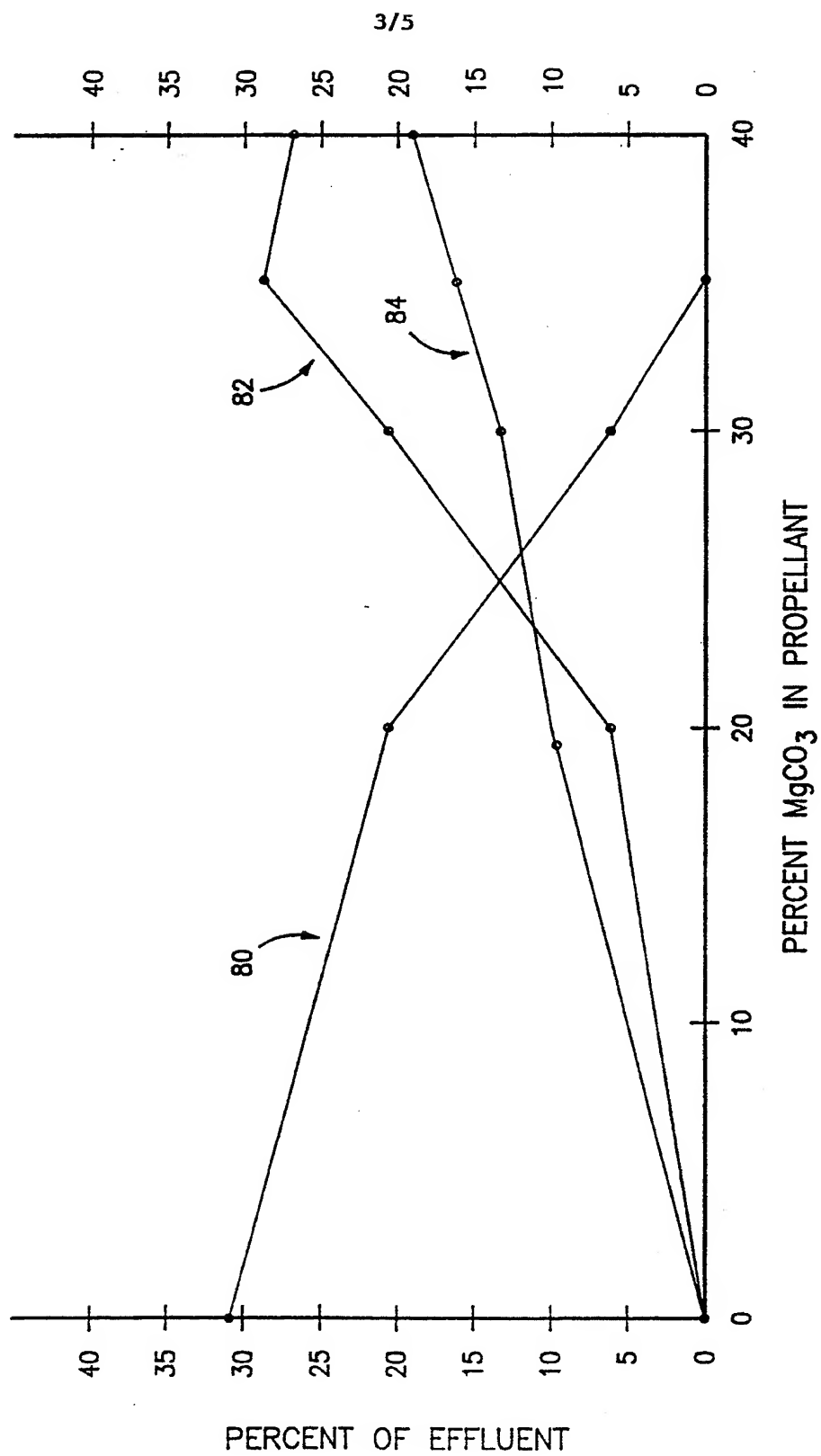


FIG-5

4/5

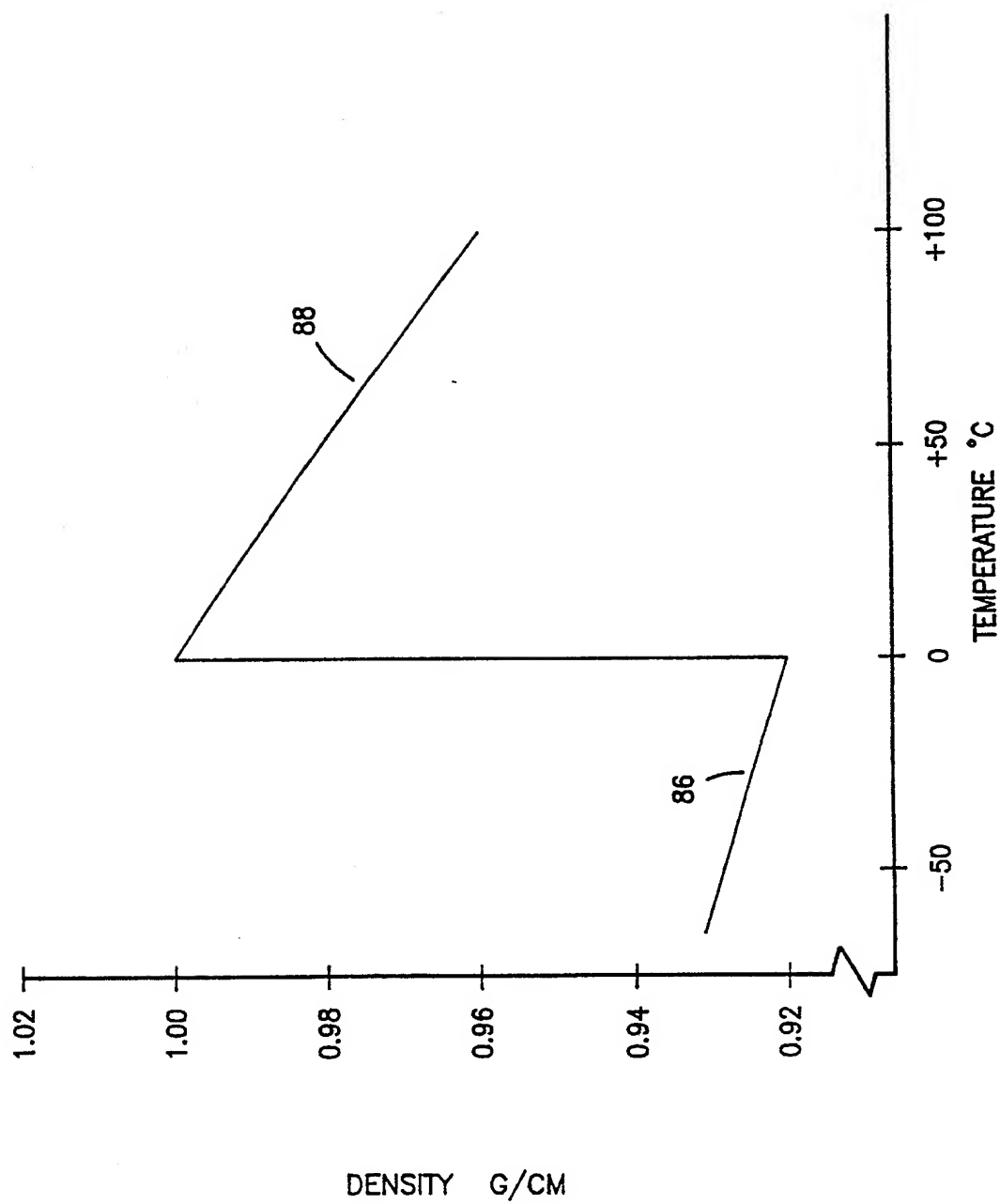


FIG-6

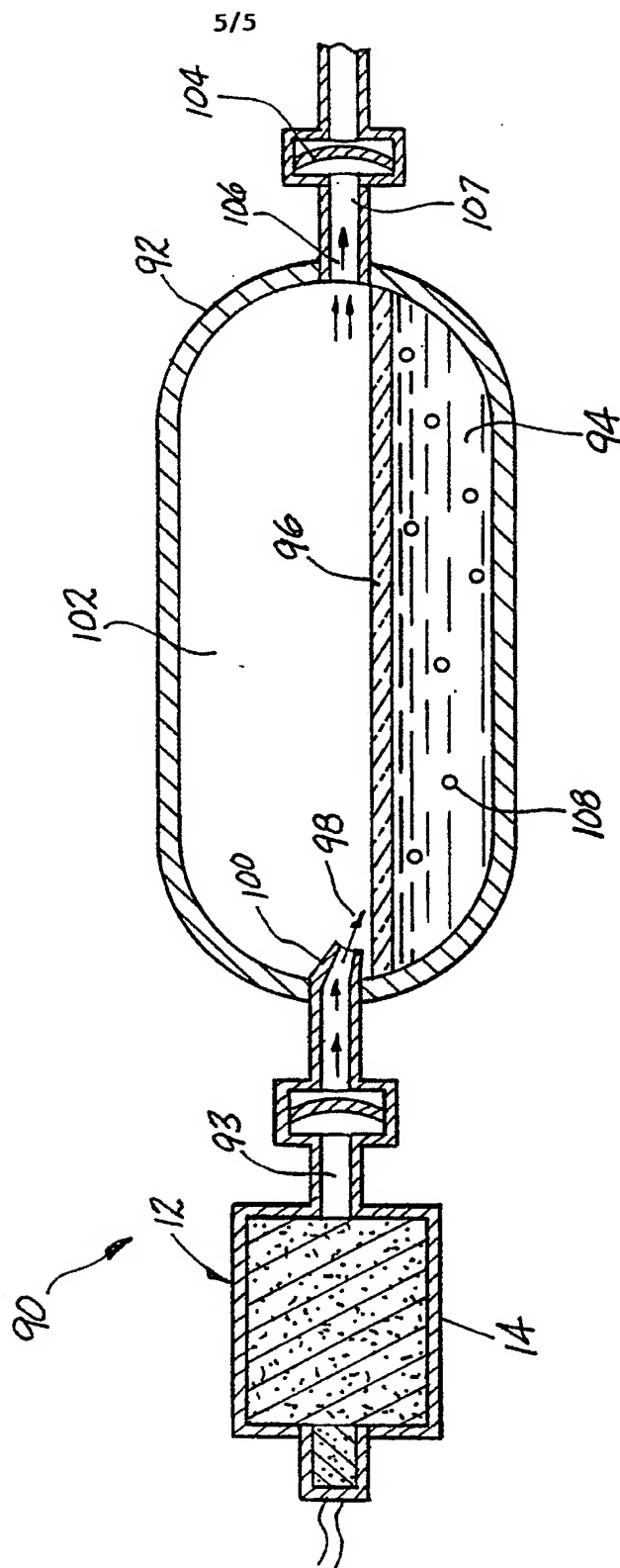


FIG-7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06622

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : A62C 35/02; C06B 45/10

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 1,648,397 (HERMANN) 08 NOVEMBER 1927	1-2, 4, 6
---	See entire document.	-----
A		20-27
Y	US, A, 3,785,674 (POOLE ET AL.) 15 JANUARY 1974	1-2, 4-5, 7
	See entire document.	3
Y	US, A, 4,319,640 (BROBEIL) 16 MARCH 1982	1-2, 4-5, 7
	See entire document.	3
Y	US, A, 4,276,938 (KLIMENKO ET AL.) 07 JULY 1981	1-2, 4-5, 7
	See entire document, especially column 4, lines 47-48.	3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 AUGUST 1994

Date of mailing of the international search report

SEP 08 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ANDREW C. PIKE

Telephone No. (703) 308-3423

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US94/06622

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US, A, 2,838,122 (HUTCHINSON) 10 JUNE 1958 See entire document.	8-9, 11 ----- 10
X --- Y	US, A, 4,601,344 (REED, JR. ET AL.) 22 JULY 1986 See entire document.	12-13 ----- 14-16, 28-32 17-19
Y	US, A, 3,901,747 (GARNER) 26 AUGUST 1975 See entire document, especially column 2, lines 48-55.	14-16, 28-32 17-19
Y	US, A, 5,035,757 (POOLE) 30 JULY 1991 See entire document, especially column 1, lines 23-30.	3 10 17-19
A	US, A, 798,142 (MYERS) 29 AUGUST 1905 See entire document.	8-19
A	US, A, 1,119,799 (BOWMAN) 08 DECEMBER 1914 See entire document.	1-7
A	US, A, 2,530,633 (SCHOLZ) 21 NOVEMBER 1950 See entire document.	1-7
A	US, A, 4,637,472 (DECIMA) 20 JANUARY 1987 See entire document.	1-7
A	US, A, 4,194,571 (MONTE) 25 MARCH 1980 See entire document	1-7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06622

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

169/ 5, 6, 7, 9, 11, 12, 26, 27, 44, 46, 61, 62, 84;
252/5, 7, 8; 149/36

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

169/ 5, 6, 7, 8, 9, 11, 12, 26, 27, 28;
169/30, 35, 43, 44, 45, 46, 47, 60, 61, 62, 71, 72, 78, 84, 85;
252/2, 3, 4, 5, 6, 7, 8; 149/19.6, 35, 36, 61, 77

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

The International Searching Authority found multiple inventions in this international application, as follows:

Invention I: Claims 1-7, drawn to an apparatus for suppressing a fire including a vaporizable liquid contained within a chamber, classified in class 169, subclass 11.

Invention II: Claims 8-11, drawn to an apparatus for suppressing a fire including a packed powder contained within a chamber, classified in class 169, subclass 9.

Invention III: Claims 12-19, drawn to an apparatus for suppressing a fire including a gas generator containing a propellant and a fire suppressant, classified in class 169, subclass 12.

Invention IV: Claims 20-27, drawn to an apparatus for suppressing a fire including a mixture of water and ice contained within a chamber, classified in class 169, subclass 5.

Invention V: Claims 28-32, drawn to a fire suppressing composition including magnesium carbonate, classified in class 252, subclass 7.

The five inventions do not share a common special technical feature. The special technical features are: of Invention I, a vaporizable liquid contained within the chamber; of Invention II, a packed powder contained within the chamber; of Invention III, the gas generator containing a propellant and a fire suppressant; of Invention IV, a mixture of water and ice contained within the chamber; and of Invention V, the fire suppressing composition including magnesium carbonate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/06622

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Telephone Practice
Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐
☒

- The additional search fees were accompanied by the applicant's protest.
No protest accompanied the payment of additional search fees.